

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. :

U.S. National Serial No. :

Filed :

PCT International Application No. : PCT/EP2003/014452

VERIFICATION OF A TRANSLATION

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Date: March 15, 2005

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WO 2004/056899

PCT/EP2003/014452

Synthetic material dispersions

The invention relates to synthetic resin dispersions for the production of hydrophilic sheet-like structures or hydrophilic shaped articles provided with hydrophobic surfaces..

The use of solutions of melamine resin precondensates or partly etherified melamine resin precondensates in water or alcohol/water mixture as coating or impregnating compositions for hydrophilic sheet-like structures is known (EP 0 686 665 A2; DE 44 20 013 A1).

A disadvantage of hydrophilic sheet-like structures, such as paper or cardboard, impregnated with conventional melamine resin solutions is their low resistance to weathering when used outdoors, since water can diffuse unimpeded into the impregnated surface layer and initiate cracking in the surface layer.

A known process for improving the resistance to weathering of hydrophilic sheet-like structures impregnated with melamine resin is the additional coating of the impregnated sheet-like structures with a hydrophobic top layer of polyvinyl fluoride (US 3 676 290 A), polyacrylates (DE 33 29 679 C1; EP 0 824 560 A1; US 3 841 956 A; DE 36 30 315 A1), unsaturated polyesters (EP 0 824 560 A1) or ethylene/propylene rubber (EP 0 206 832 A1). However, the compatibility of these hydrophobic top layers with the hydrophilic layer lying underneath is limited, so that detachment of the layer may occur during exposure to mechanical stresses.

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Melamine resin dispersions which comprise completely or partly cured melamine resin particles are furthermore known. According to US 3 945 980 A, an amine resin

precondensate is diluted, with the addition of polyvinyl alcohol, until its water miscibility limit is exceeded and is cured under acid conditions. US 5 344 704 A describes dispersions of cured ground melamine  
5 resin particles in water or melamine resin solutions. However, nanoscale dispersions and hydrophobic surfaces cannot be achieved with these dispersions.

The object of the invention is synthetic resin dispersions for the production of hydrophilic sheet-like structures or hydrophilic shaped articles provided with hydrophobic surfaces.

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It has been found, surprisingly, that hydrophilic sheet-like structures or hydrophilic shaped articles provided with hydrophobic surfaces can be produced by coating hydrophilic sheet-like structures or  
10 hydrophilic shaped articles with aminoplast dispersions which comprise hydrophobic and hydrophilic melamine resin components and hydrophobizing agents.

The inventive object has been achieved by synthetic  
15 resin dispersions which, according to the invention, comprise

- 20 a) an aqueous phase of solutions of hydrophilic melamine resin precondensates and latent curing catalysts in water or in mixtures of water and C<sub>1</sub>-C<sub>6</sub>-alcohols and
- 25 b) an organic nanophase in the form of nanodroplets and/or nanoparticles of 70 to 99 % by weight of water-insoluble etherified melamine resin precondensates which contain acid curing catalysts and hydrophobizing agents and
- 30 c) dispersing agents in a concentration of 1 to 10 % by weight, based on the total weight of the melamine resin precondensates,  
the ratio of hydrophilic melamine resin precondensates to water-insoluble etherified melamine resin precondensates in the synthetic resin dispersions being 10 : 1 to 1 : 10 and the water content of the synthetic resin dispersions  
35 being 8 to 50 % by weight.

The synthetic resin dispersions according to the invention preferably comprise 0.1 to 5 % by weight of

pigments and/or 0.1 to 5 % by weight of flameproofing agents, in each case based on the total weight of the melamine resin precondensates.

- 5 Examples of suitable pigments which can be contained in the synthetic resin dispersions according to the invention are iron oxide, isoindoline pigments

containing ester groups, anthracene fluorescent dyestuffs, carbazole-dioxazine and delta-indanthrone blue pigment.

- 5 Examples of suitable flameproofing agents which can be contained in the synthetic resin dispersions according to the invention are ammonium polyphosphate, melamine cyanurate and zinc borate.
- 10 Examples of the melamine resin precondensates in the aqueous and in the organic nanophase are melamine resin precondensates which can contain formaldehyde, acetaldehyde and/or trimethylolacetaldehyde as aldehyde components and, in addition to melamine, also
- 15 acetoguanamine and/or benzoguanamine as melamine components.

The melamine resin precondensates in the aqueous phase and in the organic nanophase of the synthetic resin

20 dispersions according to the invention are preferably melamine resin precondensates based on melamine and formaldehyde.

The concentration of the curing catalysts both in the

25 hydrophilic and in the water-insoluble melamine resin precondensates is preferably 0.05 to 3 % by weight, based on the melamine resin precondensates.

It is furthermore preferable if the molar ratio of

30 aldehyde component / melamine component in the hydrophilic melamine resin precondensates is 1.6 : 1 to 4.5 : 1 and if the concentration of the hydrophilic melamine resin precondensates in the aqueous phase is 10 to 50 % by weight.

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In a preferred embodiment, the hydrophilic melamine resin precondensates are melamine resin precondensates partly etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols and/or non-

etherified melamine resin precondensates and the mixing ratio in the mixtures of water and C<sub>1</sub>-C<sub>6</sub>-alcohols is 95 : 5 to 5 : 95.

- 5 It is particularly advantageous here if the content of hydroxyl groups which are not etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols in the melamine resin precondensates partly etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols

is 5 to 75 mol%, based on the sum of hydroxyl groups and C<sub>1</sub>-C<sub>4</sub>-alkoxy groups in the melamine resin precondensates partly etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols.

- 5 Examples of melamine resin precondensates partly etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols are precondensates which contain 2,4-bis(methoxymethylamino)-6-hydroxymethylamino-1,3,5-triazine, 2-butoxymethylamino-4,6-dihydroxymethylamino-1,3,5-triazine or 2-ethoxymethylamino-4-methoxymethylamino-6-hydroxymethylamino-1,3,5-triazine as the main component in a mixture with higher molecular weight oligomers thereof.
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- 15 Examples of non-etherified melamine resin precondensates are precondensates which contain 2,4,6-tris(hydroxymethylamino)-1,3,5-triazine, 2,4-bis(hydroxymethylamino)-6-amino-1,3,5-triazine or 2,4-bis(hydroxymethylamino)-6-(dihydroxymethyl)imino-1,3,5-triazine as the main component in a mixture with higher molecular weight oligomers thereof.
- 20

Synthetic resin dispersions in which the aqueous phase contains 1 to 20 % by weight, based on the hydrophilic melamine resin precondensates, of further water-soluble polymers and/or water-soluble polyhydric alcohols with molecular weights of 62 to 5,000 are furthermore preferred.

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- 30 The further water-soluble polymers in the aqueous phase of the synthetic resin dispersions according to the invention are preferably hydroxyalkyl (meth)acrylate copolymers, polyhydroxy esters, polyvinyl alcohol, polypropylene oxides, polycaprolactone and/or ethylene oxide/propylene oxide block copolymers.
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Examples of hydroxyalkyl (meth)acrylate copolymers as further water-soluble polymers in the aqueous phase of the synthetic resin dispersions according to the invention are hydroxy-ethyl acrylate/methyl  
5 methacrylate copolymers and acrylamide/hydroxybutyl acrylate copolymers.

Examples of polyhydroxy esters as further water-soluble polymers in the aqueous phase of the synthetic resin  
10 dispersions according to the invention are

polyhydroxy esters based on phthalic anhydride and glycerol and polyhydroxy esters based on maleic anhydride and pentaerythritol.

- 5 Examples of water-soluble polyhydric alcohols with molecular weights of 62 to 5,000 which can be contained in the aqueous phase of the synthetic resin dispersions are ethylene glycol, tripropylene glycol, hexanediol, pentaerythritol, sorbitol, polyethylene glycols and  
10 polytetrahydrofurans.

Preferred synthetic resin dispersions are those in which the water-insoluble etherified melamine resin precondensates in the organic nanophase are melamine  
15 resin precondensates completely etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols, C<sub>2</sub>-C<sub>20</sub>-diols and/or polyalkylene oxides with molecular weights of 250 to 5,000 and/or melamine resin precondensates partly etherified with C<sub>5</sub>-C<sub>18</sub>-alcohols, C<sub>2</sub>-C<sub>20</sub>-diols and/or polyalkylene oxides with molecular  
20 weights of 250 to 5,000.

Examples of the melamine resin precondensates which are completely etherified with C<sub>1</sub>-C<sub>4</sub>-alcohols and are preferably contained in the organic nanophase as water-  
25 insoluble etherified melamine resin precondensates are precondensates which contain 2,4,6-tris(methoxymethylamino)-1,3,5-triazine, 4,6-bis(ethoxymethylamino)-2-butoxymethylamino-1,3,5-triazine or 2,4,6-tris(dimethoxymethylamino)-1,3,5-  
30 triazine as the main component in a mixture with higher molecular weight oligomers thereof.

Examples of the melamine resin precondensates which are partly etherified with C<sub>5</sub>-C<sub>18</sub>-alcohols and are  
35 preferably contained in the organic nanophase as water-insoluble etherified melamine resin precondensates are dihydroxymethylamino-1,3,5-triazine or 2-octyloxymethylamino-4-hexyloxymethylamino-6-

hydroxymethyamino-1,3,5-triazine as the main component in a mixture with higher molecular weight oligomers thereof.

- 5 Examples of C<sub>2</sub>-C<sub>20</sub>-diol components which can be contained in the water-insoluble melamine resin precondensates which are completely or partly etherified with C<sub>2</sub>-C<sub>20</sub>-diols

are ethylene glycol, diglycol, octanediol and di-  
ethylene oxide adducts.

5 Examples of polyalkylene oxide components with  
molecular weights of 250 to 5,000 which can be  
contained in the water-insoluble melamine resin  
precondensates which are completely or partly  
etherified with polyalkylene oxides are polyethylene  
oxide, polypropylene oxide, ethylene oxide/propylene  
10 oxide block copolymers or polytetrahydrofurans.

Advantageous synthetic resin dispersions are those in  
which the molar ratio of aldehyde component / melamine  
component in the water-insoluble etherified melamine  
15 resin precondensates is 3 : 1 to 6 : 1 and the average  
diameter of the nanodroplets or nanoparticles is 50 to  
300 nm.

The organic nanophase preferably comprises 0.1 to 2 %  
20 by weight of stabilizers, 1 to 20 % by weight of water-  
insoluble polyhydric alcohols with molecular weights of  
134 to 5,000 and/or 1 to 30 % by weight of laminar  
silicates, in each case based on the water-insoluble  
etherified melamine resin precondensates.

25 Examples of suitable stabilizers which can be contained  
in the organic nanophase are UV stabilizers, such as 2-  
(2-hydroxy-3-tert-butyl-5-methylphenyl)benzotriazole,  
2,4-dihydroxybenzophenone, sebacic acid bis[2,2,6,6-  
30 tetramethyl-1-(octyloxy)-4-piperidinyl] ester or  
bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, and/or  
antioxidants, such as octadecyl 3-(3',5'-di-tert-butyl-  
4'-hydroxyphenyl)propionate.

35 Examples of water-insoluble polyhydric alcohols with  
molecular weights of 134 to 5,000 which can be  
contained in the organic nanophase are octanediol,

dodecanediol, octadecanediol and polypropylene glycols with molecular weights of 500 to 5,000.

5 Examples of suitable laminar silicates which can be contained in the organic nanophase are montmorillonite, bentonite, kaolinite, muscovite, hectorite, fluorohectorite, kanemite, revdite, grumantite, illerite, saponite, beidelite, nontronite,

stevensite, laponite, taneolite, vermiculite,  
halloysite, volkonskoite, magadite, rectorite,  
kenyaite, sauconite, boron fluorophlogopites and/or  
synthetic smectites.

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The hydrophobizing agents which are contained in the  
organic nanophase are preferably 30 to 1 % by weight of  
organic silicon compounds of the type of  
organosilanols, organosiloxanes, organosilanes,  
10 organoaminosilanes or polyorganosiloxanes terminated  
with amino end groups or hydroxyl end groups; surface-  
fluorinated  $\text{SiO}_2$  nanoparticles, polytetrafluoroethylene  
nanoparticles and/or ethylenically unsaturated  $\text{C}_4$ - $\text{C}_{20}$ -  
dicarboxylic acid anhydride copolymers containing imide  
15 groups.

Examples of polyorganosiloxanes terminated with amino  
end groups or hydroxyl end groups as hydrophobizing  
agents are aminopropyl-terminated polydimethylsiloxanes  
20 or hydroxybutyl-terminated polydimethylsiloxanes with  
molecular weights of 1,000 to 6,000.

Examples of organosilanols as hydrophobizing agents are  
trimethylsilanol, diethylsilanediol,  
25 triisopropylsilanol and triphenylsilanol.

Examples of organosiloxanes are  
tetramethyldisiloxanediol or tetraphenyldisiloxanediol.

30 Examples of organosilanes are tetraphenylsilane,  
vinyltrimethoxysilane and tetradodecyl-silane.

Examples of organoaminosilanes are triethylaminosilane  
and triphenylaminosilane.

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Examples of surface-fluorinated  $\text{SiO}_2$  nanoparticles are  
pyrogenic silicic acids which have average particle

diameters in the range from 5 to 30 nm and are modified by reaction with fluorinated hydrocarbons.

5     Suitable ethylenically unsaturated C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acid anhydride copolymers containing imide groups are styrene/maleic anhydride copolymers which are imidized with amines, such as octylamine, diglycolamine or ethanolamine.

Nonionic dispersing agents or mixtures of 50 to 99 % by weight of nonionic and 1 to 50 % by weight of anionic dispersing agents are advantageously employed as dispersing agents in the synthetic resin dispersions according to the invention.

Etherified melamine resin oligomers with molecular weights of 2,000 to 30,000 are preferably employed as dispersing agents in the synthetic resin dispersions.

10 Melamine resin oligomers etherified with polyethylene glycols with molecular weights of 1,000 to 8,000 and/or C1-C12-monoalkyl-etherified polyethylene glycols with molecular weights of 1,000 to 8,500 and C1-C10 alcohols are particularly advantageous.

15 In a particularly preferred embodiment the molar ratio here of polyethylene glycol / C1-C10-alcohol is 1 : 10 to 2 : 1 and the molar ratio of melamine / formaldehyde / etherifying alcohol is 1 : 2.8 : 2.5 to 1 : 4.5 : 3.5.

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These etherified melamine resin oligomers have a hydrophilic and a hydrophobic radical. For this reason they can act as a dispersing agent. The advantage over the use of conventional dispersing agents is that the melamine resin oligomers are bonded covalently and therefore permanently in sheet-like structures.

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The hydrophilic sheet-like structures are preferably laminates, pressed laminates or one-layered sheet-like carrier materials based on cellulose and/or polar plastics of the type of polyamide, polyester, polyvinyl acetate and/or polyvinyl alcohol, preferably paper.

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35 The hydrophilic shaped articles are preferably timber products, or semi-finished products or moulded materials produced by thermoplastic processing of polar plastics of the type of polyamide, polyester, polyvinyl



acetate and/or polyvinyl alcohol or by processing of blends of 55 to 90 % by weight of wood and 45 to 10 % by weight of thermoplastics and/or thermosetting plastics.

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Examples of hydrophilic shaped articles are timber profiles produced by working by cutting or turned timber objects, or products of polyamide or

polyethylene terephthalate produced by injection moulding or profile extrusion, such as cladding elements, covers or circular profiles.

- 5 Examples of thermoplastics which can be contained in the hydrophilic shaped articles of blends of 55 to 90 % by weight of wood and 45 to 10 % by weight of thermoplastics are polyethylene, polypropylene, polystyrene, polyamide 6 polymethyl methacrylate, poly-  
10 2,6-dimethylphenylene oxide and polybutylene terephthalate.

Examples of thermosetting plastics which can be contained in the hydrophilic shaped articles of blends  
15 of 55 to 90 % by weight of wood and 45 to 10 % by weight of thermosetting plastics are phenolic resins, urea resins and unsaturated polyester resins.

The latent curing catalysts contained in the aqueous  
20 phase of the synthetic resin dispersions according to the invention are preferably ammonium salts, in particular ammonium peroxydisulphate, ammonium phosphate, ammonium sulphate, ammonium chloride, ammonium oxalate and/or ammonium thiocyanate; C<sub>1</sub>-C<sub>4</sub>-  
25 alkylammonium salts of carboxylic acids, in particular methylammonium phthalate, methylammonium maleate and/or the methylamine salt of naphthalenesulphonic acid; and/or esters of phosphoric acid, phosphorous acid, oxalic acid and/or phthalic acid, in particular diethyl  
30 phosphate, oxalic acid dimethyl ester and/or phthalic acid dimethyl ester.

Acid curing catalysts which are preferably contained in the water-insoluble melamine resin precondensates of  
35 the synthetic resin dispersions according to the invention are:

- at a molar ratio of aldehyde component/melamine component up to 4 : 1, blocked sulphonic acids,

aliphatic C<sub>4</sub>-C<sub>18</sub>-carboxylic acids, alkali metal salts or ammonium salts of phosphoric acid, C<sub>1</sub>-C<sub>12</sub>-alkyl esters or C<sub>2</sub>-C<sub>8</sub>-hydroxyalkyl esters of C<sub>6</sub>-C<sub>14</sub>-aromatic carboxylic acids or inorganic acids, salts of melamine  
5 or guanamines with C<sub>1</sub>-C<sub>18</sub>-aliphatic carboxylic acids, anhydrides, half-esters or half-amides of C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acids, half-esters or half-amides of copolymers of ethylenically unsaturated C<sub>4</sub>-

C<sub>20</sub>-dicarboxylic acid anhydrides and ethylenically unsaturated monomers of the type of C<sub>2</sub>-C<sub>20</sub>-olefins and/or C<sub>8</sub>-C<sub>20</sub>-vinylaromatics, (meth)acrylic acid copolymers and/or salts of C<sub>1</sub>-C<sub>12</sub>-alkylamines or alkanolamines with C<sub>1</sub>-C<sub>18</sub>-aliphatic, C<sub>6</sub>-C<sub>14</sub>-aromatic or alkylaromatic carboxylic acids or inorganic acids of the type of hydrochloric acid, sulphuric acid or phosphoric acid, or

5 - at a molar ratio above 4 : 1, strong acids, preferably hydrochloric acid, sulphuric acid, phosphoric acid, p-toluenesulphonic acid, methanesulphonic acid, dodecylbenzenesulphonic acid, dinonylnaphthalenesulphonic acid and/or  
10 dinonylnaphthalenedisulphonic acid.

15 Examples of blocked sulphonic acids as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of aldehyde component/melamine component up to 4 : 1 are benzil  
20 monoxime tosylate,  $\alpha$ -cyclohexylsulphonyloxy-  
iminophenylacetic acid ethyl ester, acetone oxime p-benzoylbenzenesulphonate,  $\alpha$ -(4-nitrobenzene-  
sulphonyloxyimino)benzyl cyanide, 2-nitrobenzyl  
sulphonate and 2-methylsulphonyloxyimino-4-phenyl-but-  
25 3-enenitrile.

Examples of aliphatic C<sub>4</sub>-C<sub>18</sub>-carboxylic acids as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of aldehyde  
30 component/melamine component up to 4 : 1 are butyric acid, caproic acid, palmitic acid, stearic acid and oleic acid.

35 Examples of alkali metal salts or ammonium salts of phosphoric acid as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of aldehyde component/melamine component up

to 4 : 1 are ammonium hydrogen phosphate, sodium polyphosphate and potassium hydrogen phosphate.

5 Examples of C<sub>1</sub>-C<sub>12</sub>-alkyl esters or C<sub>2</sub>-C<sub>8</sub>-hydroxyalkyl  
esters of C<sub>6</sub>-C<sub>14</sub>-aromatic carboxylic acids or inorganic  
acids as acid curing catalysts in the water-insoluble  
melamine resin precondensates which have a molar ratio  
of aldehyde component/melamine component up to 4 : 1  
are dibutyl phthalate, phthalic acid diglycol ester  
10 and/or trimellitic acid glycol ester.

Examples of salts of melamine or guanamines with C<sub>1</sub>-C<sub>18</sub>-aliphatic carboxylic acids as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of aldehyde component/melamine component up to 4 : 1 are melamine formate, melamine citrate and/or acetoguanamine butyrate.

Examples of anhydrides, half-esters or half-amides of C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acids as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of aldehyde component/melamine component up to 4 : 1 are maleic anhydride, mono-C<sub>1</sub>-C<sub>18</sub>-alkyl maleates, such as maleic acid monobutyl ester, maleic acid monoethylhexyl ester or monostearyl maleate, or maleic acid mono-C<sub>1</sub>-C<sub>18</sub>-alkylamides, such as maleic acid monoethylamide, maleic acid monooctylamide or maleic acid monostearylamide.

Examples of half-esters or half-amides of copolymers of ethylenically unsaturated C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acid anhydrides and ethylenically unsaturated monomers of the type of C<sub>2</sub>-C<sub>20</sub>-olefins and/or C<sub>8</sub>-C<sub>20</sub>-vinylaromatics as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of aldehyde component/melamine component up to 4 : 1 are half-esters or half-amides of copolymers of maleic anhydride and C<sub>3</sub>-C<sub>8</sub>- $\alpha$ -olefins of the type of isobutene, diisobutene and/or 4-methylpentene and/or styrene with a molar ratio of maleic anhydride/C<sub>3</sub>-C<sub>8</sub>- $\alpha$ -olefin or styrene or corresponding monomer mixtures of 1 : 1 to 1 : 5.

Examples of salts of C<sub>1</sub>-C<sub>12</sub>-alkylamines or alkanolamines with C<sub>1</sub>-C<sub>18</sub>-aliphatic, C<sub>6</sub>-C<sub>14</sub>-aromatic or alkylaromatic carboxylic acids and inorganic acids of the type of hydrochloric acid, sulphuric acid or phosphoric acid as acid curing catalysts in the water-insoluble melamine resin precondensates which have a molar ratio of

aldehyde component /melamine component up to 4 : 1 are ethanolammonium chloride, triethylammonium maleate, diethanolammonium phosphate and/or isopropylammonium p-toluenesulphonate.

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Particularly preferred synthetic resin dispersions are those which comprise as nonionic dispersing agents ethylene oxide/propylene oxide block copolymers, poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxides monoetherified with C<sub>8</sub>-C<sub>18</sub>-  
10 alcohols,

esters of polyhydric alcohols with C<sub>8</sub>-C<sub>18</sub>-carboxylic acids, C<sub>2</sub>-C<sub>4</sub>-alkylene oxide adducts on C<sub>8</sub>-C<sub>18</sub>-fatty alcohols and/or copolymers of ethylenically unsaturated C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acid anhydrides and ethylenically unsaturated monomers of the type of C<sub>2</sub>-C<sub>20</sub>-olefins, C<sub>8</sub>-C<sub>20</sub>-vinylaromatics, C<sub>4</sub>-C<sub>21</sub>-acrylic acid esters and/or C<sub>5</sub>-C<sub>22</sub>-methacrylic acid esters, which have been imidized with poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxides terminated by amino groups.

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Examples of the poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxides which are monoetherified with C<sub>8</sub>-C<sub>18</sub>-alcohols and have molecular weights of 400 to 6,000 and are contained in the synthetic resin dispersions according to the invention as nonionic dispersing agents are polyethylene glycol monostearyl ether and polyethylene glycol monododecyl ether.

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Examples of the esters of polyhydric alcohols with C<sub>8</sub>-C<sub>18</sub>-carboxylic acids contained in the synthetic resin dispersions according to the invention as nonionic dispersing agents are sorbitan fatty acid esters and polyethylene glycol glyceryl-stearate.

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Examples of the C<sub>2</sub>-C<sub>4</sub>-alkylene oxide adducts on C<sub>8</sub>-C<sub>18</sub>-fatty alcohols contained in the synthetic resin dispersions according to the invention as nonionic dispersing agents are oxyethylated fatty alcohols and oxyethylated oxo-alcohols.

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Examples of the copolymers of ethylenically unsaturated C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acid anhydrides and ethylenically unsaturated monomers of the type of C<sub>2</sub>-C<sub>20</sub>-olefins, C<sub>8</sub>-C<sub>20</sub>-vinylaromatics, C<sub>4</sub>-C<sub>21</sub>-acrylic acid esters and/or C<sub>5</sub>-C<sub>22</sub>-methacrylic acid esters which have been imidized with amino-terminated poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxides and are contained in the synthetic resin dispersions according to the invention as nonionic dispersing

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agents are maleic anhydride/styrene copolymers or maleic anhydride/ $\alpha$ -methylstyrene/butyl acrylate copolymers imidized with  $\alpha$ -amino-terminated polyethylene oxides.

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Examples of anionic dispersing agents in the synthetic resin dispersions according to the invention are alkyl sulphates, oxyethylated alkyl sulphates, ether sulphates, alkanesulphonates, olefinsulphonates and

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alkylnaphthalenesulphonates.

Preferred anionic dispersing agents in the synthetic resin dispersions according to the invention are alkali metal salts of (meth)acrylic acid copolymers, salts of oxyethylated C<sub>6</sub>-C<sub>18</sub>-alkylphenol-sulphates and/or alkali metal and/or ammonium salts of C<sub>8</sub>-C<sub>18</sub>-carboxylic acids and/or C<sub>8</sub>-C<sub>18</sub>-alkylsulphonates.

Examples of the salts of oxyethylated C<sub>6</sub>-C<sub>18</sub>-alkylphenol sulphates optionally contained in the synthetic resin dispersions according to the invention as anionic dispersing agents are oxyethylated sodium p-nonylphenol-sulphate and oxyethylated sodium p-dodecylphenol-sulphate.

Examples of the alkali metal and/or ammonium salts of C<sub>8</sub>-C<sub>18</sub>-carboxylic acids optionally contained in the synthetic resin dispersions according to the invention as anionic dispersing agents are sodium oleate and ammonium palmitate.

The synthetic resin dispersions for the production of hydrophilic sheet-like structures or hydrophilic shaped articles provided with hydrophobic surfaces are prepared by a multi-stage process in which

- in the first process stage mixtures of hydrophilic melamine resin precondensates, water-insoluble melamine resin precondensates and hydrophobizing agents are homogenized as highly viscous liquids or melts at 50 to 130°C over residence times of 2 to 15 minutes and
- in the second process stage the mixtures are introduced at high shear rates over residence times of 3 minutes to 15 minutes into 8.7 to 100 % by weight, based on the sum of the melamine resin precondensates, of water which contains 0.5 to 10 % by weight, based on the sum of the melamine resin precondensates, of dispersing agents and the

dispersions are cooled to room temperature at low shear rates, with further stirring, latent curing agents and acid curing catalysts being added after the cooling to room temperature.

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It is preferable here if the water in the second process stage contains 1 to 25 % by weight, based on the total weight of the melamine resin precondensates, of C<sub>3</sub>-C<sub>6</sub>-

alcohols as dispersing auxiliaries and/or water-soluble polymers and/or water-soluble polyhydric alcohols and is heated to temperatures up to 90°C, and if pigments and/or flameproofing agents are added after the cooling to room temperature.

A second process for the preparation of the synthetic resin dispersions according to the invention is a multi-stage process in which

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- in the first process stage water-insoluble melamine resin precondensates are introduced as highly viscous liquids or melts at 50 to 130°C at high shear rates over residence times of 3 minutes to 15 minutes into 8.7 to 100 % by weight, based on the water-insoluble melamine resin precondensates, of water which contains 0.5 to 10 % by weight, based on the water-insoluble melamine resin precondensates, of dispersing agents and the dispersions are cooled to room temperature at low shear rates, with further stirring, and
- in the second process stage hydrophilic melamine resin precondensates are added as solutions to the aqueous dispersion of the water-insoluble melamine resin precondensates and the mixture is homogenized, latent curing agents and acid curing catalysts being added to the aqueous solutions.

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It is preferable here if the water-insoluble melamine resin precondensates in the first process stage and/or the aqueous solutions of the second process stage contain up to 30 % by weight of hydrophobizing agent and the water in the first process stage contains 1 to 25 % by weight, based on the water-insoluble melamine resin precondensates, of C<sub>3</sub>-C<sub>6</sub>-alcohols as dispersing auxiliaries and/or water-soluble polymers and/or water-soluble polyhydric alcohols and is heated to temperatures up to 90°C, and if pigments and/or

- 14a -

flameproofing agents are added to the aqueous solutions of the second process stage.

In a further multi-stage process for the preparation of the synthetic resin dispersions according to the invention

- 5       - in the first process stage melamine resins etherified with C1-C10-alcohols are reacted, in the presence or in the absence of acid curing catalysts, with polyethylene glycols with molecular weights of 500 to 8,000 at temperatures of 50 to 165°C to give etherified melamine resin oligomers,
- 10       - in the second process stage, at temperatures of 60 to 200°C, mixtures of 15 to 40 % by weight of etherified melamine resin oligomers and 85 to 60 % by weight of melamine resins etherified with C1-C10-alcohols and with molecular weights of 300 to 800 are introduced at a high shear gradient into water, which is preheated to 20 to 80°C, 0 to 8 % by weight of hydrophobizing agent being added to the melt of etherified melamine resin oligomers and melamine resins etherified with C1-C10-alcohols and/or the aqueous phase in the second process stage, and
- 15       - in the third process stage 10 to 40 % by weight of hydrophilic melamine resin precondensates are mixed in the form of a 30 to 70 % strength aqueous solution with 90 to 60 % by weight of the mixture of melamine resin oligomers and etherified melamine resins of the second process stage.
- 20
- 25
- 30       For all three process variants, suitable dispersing units with a high shear action are in-line dispersers with a circulation, stirred reactors with high-performance dispersers for stirring speeds up to 25,000 revolutions per minute or ultrasonic dispersers.

35

The invention furthermore relates to hydrophilic sheet-like structures or hydrophilic shaped articles which

are provided with hydrophobic surfaces and are produced using the synthetic resin dispersions described above.

5 The application of the synthetic resin dispersions according to the invention to the hydrophilic sheet-like structure can be carried out by conventional application processes, such as roller application, doctor blade application, fluidized bed coating, dip coating, brushing and

spraying processes and electrostatic spraying. Favourable drying and curing temperatures are in the range from 100 to 220°C.

- 5 During the application and drying operation, a substantial concentration of the organic nanophase takes place at the coating surface, so that after drying and curing the coating surface virtually exclusively comprises crosslinked melamine resins based  
10 on the water-insoluble etherified melamine resin precondensates. The hydrophobic surface layer produced on the hydrophilic sheet-like structures or hydrophilic shaped articles has a high adhesive strength on the hydrophilic sheet-like structures, since during the  
15 crosslinking operation it is linked chemically to the melamine resins which are based on the hydrophilic melamine resin precondensates and are absorbed into the hydrophilic sheet-like structures.
- 20 The thickness of the hydrophobic surfaces of the hydrophilic sheet-like structures or hydrophilic shaped articles provided with hydrophobic surfaces is preferably 1 to 40  $\mu\text{m}$ .
- 25 Thin layer thicknesses of the hydrophobic surfaces on the hydrophilic sheet-like structures or hydrophilic shaped articles have the effect in the case of rough surfaces of good gluing properties of the products and an adequate permeability to water vapour.
- 30 In the production of the hydrophobic surfaces on the hydrophilic sheet-like structures, excluding laminates, or hydrophilic shaped articles, the synthetic resin dispersions are preferably applied by spraying on after  
35 preheating of the hydrophilic sheet-like structures or hydrophilic shaped articles to 50 to 95°C, and the sheet-like structures or shaped articles impregnated with the synthetic resin dispersions are dried and



cured at 100 to 145°C. It is of particular advantage to carry out the drying and curing by infra-red irradiation of the impregnated sheet-like structures or shaped articles.

5

In the case of production of laminates based on hydrophilic sheet-like structures coated with hydrophobic surfaces, curing is preferably carried out by

conventional pressing technology under pressures of 30 to 150 bar at temperatures in the range from 140 to 170°C.

- 5 In the case of shaped articles, such as profiles, which are produced by extrusion of blends of 55 to 90 % by weight of wood and 45 to 10 % by weight of thermoplastics or thermosetting plastics, or polar plastics of the type of polyamide, polyester, polyvinyl acetate and/or polyvinyl alcohol, for production of the hydrophobic surfaces it is of advantage to spray the synthetic resin dispersions on to the profile directly after the extruder die.
- 10
- 15 Preferred fields of use of the sheet-like structures or shaped articles coated with synthetic resin dispersions are uses in the construction sector, in particular as cladding panels, and in the sport and leisure sector where an improved resistance to weathering and the ability to be glued are required.
- 20

The invention is explained by the following examples:

#### Example 1

- 25 330 g of a hydrophilic melamine-formaldehyde precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded methanol 1 : 3 : 2.1, which contains 30 g of isobutanol, as a hydrophilic melamine resin precondensate, are melted at 120°C in a 2.5 l stirred reactor with the addition of 100 g of an imidized styrene/maleic anhydride copolymer (molar ratio of styrene/maleic anhydride 2 : 1, imidized with a mixture of 70 mol% of octylamine and 30 mol% of diglycolamine), as a hydrophobizing agent, and the components are homogenized.
- 30
- 35

600 g of a water-insoluble melamine resin precondensate which contains 2,4,6-tris(methoxy-methylamino)-1,3,5-triazine as the main component in a mixture with the corresponding higher molecular weight oligomers are  
5 metered into the low-viscosity melt in the course of 20 minutes at 100°C and the components are homogenized.

The homogeneous melt obtained is dispersed in the course of 15 minutes in a 2.5 l stirred reactor with a  
10 high-speed disperser (Ultra-Turrax,

Janke&Kunkel, Staufen), which contains 990 g of water and 18 g of a 75:25 dispersing agent mixture of an oxyethylated C<sub>16</sub>-C<sub>18</sub>-alcohol mixture (80 mol of ethylene oxide/mol of alcohol) and an oxyethylated sodium pnonylphenol-sulphate (ethylene oxide content 23 % by weight) at 70°C, and, after the emulsion has cooled to 35°C, 100 g of butanol, as a dispersing auxiliary, 1.2 g of methylammonium phthalate, as a latent curing agent, and 8 g of monostearyl maleate, as an acid curing catalyst, are added.

The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 130 nm.

For production of a decorative paper (weight per unit area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 98 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.9 % by weight, the decorative paper has a resin content of 56 % by weight.

A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 45 % by weight of melamine-formaldehyde precondensate, molar ratio of melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at 155°C for 180 seconds.

The contact angle of distilled water on the laminate surface is 102 degrees.

If in a comparison experiment the hydrophilic melamine-formaldehyde precondensate partly etherified with methanol (molar ratio of melamine/formaldehyde/bonded methanol 1 : 3 : 2.1) is applied, after addition of 1 %  
5 by weight, based on the precondensate, of methylammonium phthalate, as a latent curing agent, to the decorative paper surface, analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the

melamine resin precondensates of 75 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.9 % by weight and lamination with kraft paper, the contact angle of distilled water on the surface of the laminate produced under analogous conditions is 69 degrees.

#### Example 2

10 A mixture of 250 g of a hydrophilic melamine-formaldehyde precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded methanol 1 : 3 : 2.1, which contains 30 g of isobutanol, is melted at 95°C in a 2.5 l stirred  
15 reactor with the addition of 75 g of an imidized styrene/maleic anhydride copolymer (molar ratio of styrene/maleic anhydride 2.6 : 1, imidized with a mixture of 60 mol% of octylamine and 40 mol% of ethanolamine), as a hydrophobizing agent, and the  
20 components are homogenized. 500 g of a water-insoluble etherified melamine resin precondensate which contains bis-2,4(dodecyloxy-methylamino)-6-hydroxymethylamino-1,3,5-triazine as the main component in a mixture with higher molecular weight oligomers are metered into the  
25 low-viscosity melt in the course of 15 minutes at 95°C and the components are homogenized.

The homogeneous melt obtained is dispersed in the course of 15 minutes in a 2.5 l stirred reactor with a  
30 high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen), which contains 950 g of water and 24 g of an oxyethylated cetyl alcohol/stearyl alcohol mixture (27 mol of ethylene oxide/mol of alcohol, molecular weight about 1,450) at 30°C, and, after the emulsion has  
35 cooled to 20°C, 80 g of isobutanol, as a dispersing auxiliary, 3 g of ammonium oxalate, as a latent curing agent, and 5.4 g of acetoguanamine butyrate, as an acid curing catalyst, are added.

The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 55 nm.

- 5 For production of a decorative paper (weight per unit area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the decorative paper surface by ATR spectroscopy results in
- 10 a content of etherified hydroxyl groups

of the melamine resin precondensates of 70 mol%. After drying in a circulating air oven at 140°C to a volatile content of 6.1 % by weight, the decorative paper has a resin content of 59 % by weight.

5

A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 45 % by weight of melamine-formaldehyde precondensate, molar ratio of  
10 melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at 155°C for 180 seconds.

The contact angle of distilled water on the laminate  
15 surface is 102 degrees.

If in a comparison experiment a hydrophilic melamine-formaldehyde precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded  
20 methanol 1 : 3 : 2.1, which contains 30 g of isobutanol, is applied, after addition of 1 % by weight, based on the precondensate, of ammonium oxalate, as a latent curing agent, to the decorative paper surface, analysis of the decorative paper surface  
25 by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 51 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.9 % by weight and lamination with kraft paper, the contact angle of  
30 distilled water on the surface of the laminate produced under analogous conditions is 65 degrees.

### Example 3

35 A mixture of 260 g of a hydrophilic melamine-formaldehyde precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded methanol 1 : 5 : 3.2, 600 g of a water-insoluble



precondensate which contains 2,4-bis(methoxymethylamino)-6-butoxymethyl-amino-1,3,5-triazine as the main component in a mixture with higher molecular weight oligomers, and 40 g of  
5 polytetrafluoroethylene particles (average particle diameter 30 nm) is melted at 90°C in a 2.5 l stirred reactor and the components are homogenized.

The melt obtained is dispersed in the course of 5 minutes in a 2.5 l stirred reactor with a high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen), which contains 850 g of water and 17 g of oxyethylated oleyl alcohol (80 mol of ethylene oxide/mol of oleyl alcohol) at 65°C, and, after the emulsion has cooled to 35°C, 2.9 g of ammonium phosphate, as a latent curing agent, and 8 g of phthalic acid diglycol ester, as an acid curing catalyst, are added.

10

The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 55 nm.

15

For production of a decorative paper (weight per unit area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 95 mol%. After drying of the decorative film in a circulating air oven at 140°C to a volatile content of 5.7 % by weight, the decorative paper has a resin content of 58 % by weight.

25

A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 45 % by weight of melamine-formaldehyde precondensate, molar ratio of melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at 160°C for 150 seconds.

30

The contact angle of distilled water on the laminate surface is 94 degrees.

35

If in a comparison experiment a hydrophilic melamine-formaldehyde precondensate partly etherified with

methanol, molar ratio of melamine/formaldehyde/bonded  
methanol 1 : 5 : 3.2, which contains 1 % by weight,  
based on the precondensate, of ammonium phosphate, as a  
latent curing agent, is applied to the decorative paper  
5 surface, analysis of the decorative paper surface by  
ATR spectroscopy results in a content of etherified  
hydroxyl groups of the

melamine resin precondensates of 65 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.7 % by weight, a contact angle of distilled water on the surface of the laminate produced under analogous conditions is 58 degrees results.

#### Example 4

A mixture of 320 g of a hydrophilic melamine-formaldehyde precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded methanol 1 : 3 : 2.1, 650 g of a water-insoluble melamine resin precondensate, which contains 2,4-bis(dioctyloxymethyl-imino)-6-hydroxy-methylamino-1,3,5-triazine as the main component in a mixture with higher molecular weight oligomers, and 35 g of hydroxypropyl-terminated polydimethylsiloxane (molecular weight 3,000) is melted at 100°C in a 2.5 l stirred reactor and the components are homogenized.

The homogeneous melt obtained is dispersed in the course of 8 minutes in a 2.5 l stirred reactor with a high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen), which contains 810 g of water and 24 g of a propylene oxide/ethylene oxide block copolymer (ethylene oxide content 77 % by weight) at 50°C, and, after the emulsion has cooled to 20°C, 3 g of ammonium peroxydisulphate, as a latent curing agent, and 3.5 g of p-toluenesulphonic acid, as an acid curing catalyst, are added.

The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 90 nm.

For production of a decorative paper (weight per unit area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the

decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 72 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.9 % by weight, the decorative paper has a resin content of 56 % by weight.

A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 45 % by weight of melamine-formaldehyde precondensate, molar ratio of  
5 melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at 155°C for 130 seconds.

The contact angle of distilled water on the laminate  
10 surface is 101 degrees.

If in a comparison experiment a hydrophilic melamine-formaldehyde precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded  
15 methanol 1 : 3 : 2.1, which contains 1 % by weight, based on the precondensate, of ammonium peroxydisulphate, as a latent curing agent, is applied to the decorative paper surface, analysis of the decorative paper surface by ATR spectroscopy results in  
20 a content of etherified hydroxyl groups of the melamine resin precondensates of 64 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.7 % by weight, a contact angle of distilled water on the surface of the laminate produced under analogous  
25 conditions is 57 degrees results.

#### Example 5

330 g of a hydrophilic melamine-formaldehyde  
30 precondensate partly etherified with methanol, molar ratio of melamine/formaldehyde/bonded methanol 1 : 3 : 2.1, which contains 30 g of isobutanol, as a hydrophilic melamine resin precondensate, are melted at 108°C in a 2.5 l stirred reactor with the addition of  
35 12.3 g of aminopropyl-terminated polydimethylsiloxane (molecular weight 3,000, amine content 1.1 mol%), as a hydrophobizing agent, and the components are homogenized. 600 g of a water-insoluble melamine resin

precondensate which contains 2,4,6-tris(methoxy-methylamino)-1,3,5-triazine as the main component in a mixture with the corresponding higher molecular weight oligomers are metered into the low-viscosity melt in  
5 the course of 20 minutes at 108°C and the components are homogenized.

The homogeneous melt obtained is dispersed in the course of 15 minutes in a 2.5 l stirred reactor with a high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen), which contains 990 g of water and 18 g of a  
5 75:25 dispersing agent mixture of an oxyethylated C<sub>16</sub>-C<sub>18</sub>-alcohol mixture (80 mol of ethylene oxide/mol of alcohol) and an oxyethylated sodium p-nonylphenol-sulphate (ethylene oxide content 23 % by weight) at 70°C, and, after the emulsion has cooled to 35°C, 100 g  
10 of butanol, as a dispersing auxiliary, 1,2 g of methylammonium phthalate, as a latent curing agent, and 8 g of monostearyl maleate, as an acid curing catalyst, are added.

15 The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 50 nm.

For production of a decorative paper (weight per unit  
20 area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine  
25 resin precondensates of 98 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.9 % by weight, the decorative paper has a resin content of 56 % by weight.

30 A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 45 % by weight of melamine-formaldehyde precondensate, molar ratio of melamine/formaldehyde 1 : 1.65) in a Collin laboratory  
35 press with a specific pressure of 90 bar at 155°C for 170 seconds.



The contact angle of distilled water on the laminate surface is 108 degrees.

If in a comparison experiment the hydrophilic melamine-  
5 formaldehyde precondensate partly etherified with  
methanol (molar ratio of melamine/formaldehyde/bonded  
methanol 1 : 3 : 2.1) is applied, after addition of 1 %  
by weight, based on the precondensate, of  
methyllumonium phthalate, as a latent curing agent, to  
10 the decorative paper surface,

analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 74 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.9 % by weight and lamination with kraft paper, the contact angle of distilled water on the surface of the laminate produced under analogous conditions is 68 degrees.

#### 10 Example 6

360 g of a low molecular weight melamine-formaldehyde precondensate completely etherified with methanol (molar ratio of melamine/formaldehyde/methanol = 1:3:3) are melted at 105°C in a 2.5 l stirred reactor with the addition of 20 g of surface-fluorinated highly disperse silicic acid (average particle size 12 nm) and the mixture is mixed as a melt into 355 g of water, which has been heated to 45°C and contains 6.5 g of an oxyethylated C<sub>16</sub>-C<sub>18</sub>-alcohol mixture (80 mol of ethylene oxide per mol of alcohol), as a dispersing agent, by means of a high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen). After cooling to 28°C, first 80 g of a 50 % strength aqueous mixture of a precondensate based on a melamine-formaldehyde impregnating resin (molar ratio of melamine/formaldehyde = 1:1.69) and finally also 1.15 g of a block copolymer of ethylene oxide and dimethylsiloxane (ethylene oxide content approx. 20 % by weight; molecular weight about 950) are added and the components are distributed homogeneously. A storage-stable low-viscosity mixture is formed and, after addition of 2.5 g of maleic acid, is used as an impregnating resin for decorative paper.

35

The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 120 nm.

For production of a decorative paper (weight per unit area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the  
5 decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 99 mol%. After drying in a circulating air oven at

140°C to a volatile content of 5.4 % by weight, the decorative paper has a resin content of 48 % by weight.

5 A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 48 % by weight of melamine-formaldehyde precondensate, molar ratio of melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at 150°C for  
10 180 seconds.

The contact angle of distilled water on the laminate surface is 98 degrees.

#### Example 7

15 The preparation of the emulsion according to example 6 is repeated. However, 3.5 g of the ethylene oxide/dimethylsiloxane block copolymer are added at the same batch size. 3.5 g of maleic acid monobutyl ether  
20 instead of maleic acid, as a curing agent, are now added to 400 g of this emulsion using a high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen). 400 g of this emulsion are mixed with 800 g of a 50 % strength aqueous precondensate solution based on a non-  
25 etherified melamine-formaldehyde impregnating resin (molar ratio of melamine/formaldehyde = 1:1.65) using a simple stirrer and the mixture is employed directly for impregnating a decorative paper (weight per unit area 110 g/m<sup>2</sup>).

30 The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 125 nm.

Analysis of the decorative paper surface by ATR  
35 spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 98 mol%. After drying in a circulating air oven at

140°C to a volatile content of 5.5 % by weight, the decorative paper has a resin content of 51 % by weight.

5 A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 48 % by weight of melamine-formaldehyde precondensate, molar ratio of melamine/formaldehyde 1 : 1.65) in a

Collin laboratory press with a specific pressure of 90 bar at 150°C for 180 seconds.

5 The contact angle of distilled water on the laminate surface is 96 degrees.

#### Example 8

10 The emulsion was prepared analogously to example 6, but no polysiloxane block copolymer and maleic acid were added.

90 g of a 1:1 mixture of an imidized styrene/maleic anhydride copolymer (molar ratio of styrene/MSA = 2:1; 15 imidized with a mixture of 60 mol% dodecylamine and 40 mol% ethanolamine) and dipropylene glycol monobutyl ether are added to 360 g of the etherified resin according to example 6 and the mixture is melted at 110°C. Thereafter, the procedure is the same as in 20 example 6. The low-viscosity stable emulsion is then mixed with 600 g of a 50 % strength aqueous precondensate solution based on a non-etherified impregnating resin (molar ratio of melamine/formaldehyde = 1:1.65) using a simple stirrer 25 and the mixture is employed directly for impregnating a decorative paper (weight per unit area 80 g/m<sup>2</sup>). The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 95 nm. Maleic acid monobutyl ether is 30 employed as the curing agent in an amount of 3 g (0.6 % by weight, based on the total resin solids).

Analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine resin precondensates of 35 97 mol%. After drying in a circulating air oven at 140°C to a volatile content of 5.4 % by weight, the decorative paper has a resin content of 50 % by weight.

A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area 180 g/m<sup>2</sup>, resin content 48 % by weight of melamine-formaldehyde precondensate, molar ratio of  
5 melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at 150°C for 180 seconds.

The contact angle of distilled water on the laminate surface is 94 degrees.

#### Example 9

5

360 g of a low molecular weight melamine-formaldehyde precondensate completely etherified with methanol (molar ratio of melamine/formaldehyde/methanol = 1:3:3) are melted at 110°C in a 2.5 l stirred reactor and are  
10 mixed as a melt into 365 g of water, which has been heated to 50°C and contains 6 g of an oxyethylated C<sub>16</sub>-C<sub>18</sub>-alcohol mixture (72 mol of ethylene oxide per mol of alcohol), as a dispersing agent, by means of a high-speed disperser (Ultra-Turrax, Janke&Kunkel, Staufen).  
15 After cooling to 25°C, first 70 g of a 50 % strength aqueous mixture of a precondensate based on a melamine-formaldehyde impregnating resin (molar ratio of melamine/formaldehyde = 1:1.8) and finally also 10 g of an aqueous dispersion of polytetrafluoroethylene  
20 nanoparticles (solids content 60 % by weight, average particle diameter 75 nm) are added and the components are distributed homogeneously. A storage-stable low-viscosity mixture is formed and, after addition of 3 g of maleic acid, is used as an impregnating resin for  
25 decorative paper.

The average particle size of the nanophase in the dispersion, determined with a particle size detector (Zeta-Sizer), is 105 nm.

For production of a decorative paper (weight per unit  
30 area 80 g/m<sup>2</sup>) provided with a hydrophobic surface, the decorative paper is coated with the synthetic resin dispersion by means of a doctor blade. Analysis of the decorative paper surface by ATR spectroscopy results in a content of etherified hydroxyl groups of the melamine  
35 resin precondensates of 98 mol%. After drying in a circulating air oven at 145°C to a volatile content of 5.2 % by weight, the decorative paper has a resin content of 52 % by weight.



A layer of the coated decorative paper is subsequently pressed together with 3 layers of core paper (weight per unit area  $180 \text{ g/m}^2$ , resin content 48 % by weight of melamine-formaldehyde precondensate, molar ratio of  
5 melamine/formaldehyde 1 : 1.65) in a Collin laboratory press with a specific pressure of 90 bar at  $155^\circ\text{C}$  for 200 seconds.

The contact angle of distilled water on the laminate surface is 106 degrees.

#### Example 10

5

Sawdust (residual moisture content 7 % by weight, average particle diameter 100  $\mu\text{m}$ , composition 90 % by weight of spruce and 10 % by weight of fir, pH 5.5 at 100 g/l in  $\text{H}_2\text{O}$  and 20°C) at 6.2 kg/hour and a  
10 butene/ethylene copolymer modified with 0.2 % by weight of maleic anhydride (melt index 0.85 g/10 minutes at 190°C/5 kg, average particle size 0.08 mm) at 3.8 kg/hour are metered into the feed hopper of a  
15 Werner&Pfleiderer ZSK 30 extruder with vacuum devolatilization, profile die 6 x 6 mm and belt take-off device, temperature profile 90/140/185/210/200/165, and the mixture is melted, homogenized, devolatilized and discharged as a square profile. Before being laid  
20 on the belt take-off device, the square profile is passed through an annular nozzle spray head and coated with the synthetic resin dispersion according to example 1.

25 The contact angle of distilled water on the surface of the coated square profile from the sawdust/polyolefin blend is 90 degrees.